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ANALYSIS OF TECHNIQUES OF SAMPLE ATTACK FOR SOIL AND MINERAL ANALYSIS - PHASE II

by

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ABSTRACT

Four methods of sample attack were evaluated in the laboratory for use in the determination of uranium, radium-226, thorium-232, thorium-230, thorium-228, and lead-210. The methods evaluated were:

(1) KF/pyrosulfate fusion

(2) Sodium carbonate fusion

(3) Nitric, perchloric, hydrofluoric acid digestion

(4) combination nitric, perchloric, hydrofluoric acid/pyrosulfate fusion.

Five samples were choosen for evaluation; two were mine tailings from Bancroft, Ontario and Beaverlodge, Saskatchewan, one was a synthetic uranium ore-silica mixture and two were soil samples supplied by AECB.

The results show that, with all samples, all methods gave consistent and accurate results for radium-226 whereas for uranium determination method (1) and (3) gave the highest recoveries. The most accurate thorium results were obtained when the method of sample dissolution was the KF/pyrosulfate or sodium carbonate fusion methods. The most accurate results for lead-210 were obtained using the three acid/pyrosulfate combination.

Among the interesting observations was the fact that the loss of lead-210 by electroplating onto platinum crucibles was not as large as suggested in the literature.

The KF/pyrosulfate dissolution procedure was found to be the fastest and, overall, most accurate dissolution method for the analysis of 1-20 samples. For larger numbers of samples the three acid/pyrosulfate fusion combination was shown to have some merit.

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RÉSUMÉ

Le présent rapport évalue quatre techniques d'attaque des échantillons utilisées pour déterminer la présence d'uranium, de radium 226, de thorium 232, de thorium 230, de thorium 238 et de plomb 210 :

(1) la fusion avec du fluorure de potassium et du pyrosulfate;
(2) la fusion avec du carbonate de soude;
(3) la digestion avec de l'acide nitrique, de l'acide perchlorique et de l'acide fluorhydrique; et
(4) la combinaison de la digestion avec de l'acide nitrique, de l'acide perchlorique et de l'acide fluorhydrique, et de la fusion avec du pyrosulfate.

Cinq échantillons ont été évalués : les deux premiers provenaient de résidus de la mine de Bancroft (Ontario) et de ceux de la mine de Beaverlodge (Saskatchewan); le troisième était un mélange synthétique de minerai d'uranium et de silice et les deux derniers étaient des échantillons de sol fournis par la CCEA.

Tous les échantillons choisis et toutes les techniques utilisées ont donné des résultats cohérents et exacts dans le cas du radium 226, tandis que les techniques de détermination n° 1 et n° 3 ont indiqué les meilleurs résultats dans le cas de l'uranium. En ce qui concerne le thorium, c'est la technique de dissolution des échantillons par fusion avec du pyrosulfate ou du carbonate de soude qui a donné les meilleurs résultats. Quant au plomb 210, c'est en combinant la technique des trois acides et du pyrosulfate que l'on a obtenu les meilleurs résultats.

Parmi les observations les plus intéressantes de l'étude, il faut signaler le fait que la perte de plomb 210 due au plaquage par galvanoplastie sur des creusets de platine n'a pas été aussi importante que la documentation existante le laissait entendre.

Le rapport conclut que la technique de dissolution faisant appel à la fusion du fluorure de potassium et du pyrosulfate s'est avérée la plus rapide et, en général, la plus précise pour l'analyse de vingt échantillons au maximum. Pour les analyses plus importantes, la technique de combinaison des trois acides et du pyrosulfate comportait certains avantages.

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A. INTRODUCTION

As a result of a literature review entitled "Analysis of Techniques of Sample Attack For Soil and Mineral Analysis" an experimental program was undertaken to investigate some of the suggestions that appeared there. For example, information regarding the fraction of sample dissolved, fraction of each element recovered, and length of time required is rarely reported. The absence of this information is due to its dependence on the type of sample being analysed, the chemical composition of the sample, the element or radionuclide being determined, and the procedure being used subsequent to the sample dissolution. Attempts were made during this study to obtain this information.

The experimental program was divided into several parts:

(1) Four methods of sample attack were tested. They were:

(a) potassium fluoride/pyrosulfate fusion,

(b) sodium carbonate fusion,

(c) $HF/HNO_3/HClO_4$ digestion and

(d) $HF/HNO_3/HClO_4$/pyrosulfate fusion.

Six replicates of five samples were subjected to each dissolution technique.

(2) The solutions resulting from each dissolution were analysed for U, ^{226}Ra, ^{232}Th, ^{230}Th, ^{228}Th and ^{210}Pb.

(3) The samples choosen were three CANMET standard mine tailings samples[1], UTS-1, UTS-3 and UTS-5 in addition to two samples provided by AECB, numbered 2218 and 2220.

B. SAMPLE DESCRIPTIONS

UTS-1 originated from Madewaska Mines mill tailings, Bancroft, Ontario.

UTS-3 originated from the Beaverlodge Saskatchewan operations of Eldorado Nuclear Ltd.

UTS-5 was a synthetic blend of a CANMET-EMR reference ore (DL-1a) and silica.

AECB 2228 and AECB 2230 were samples provided by AECB.

C. ANALYTICAL METHODOLOGIES

1. Sample Dissolution

1.1 Potassium Fluoride-Pyrosulfate Fusion Procedure

1.1.1 Apparatus

Platinum dishes: evaporating type, 40 or 50 ml, approximately 50-mm diameter by 25-mm high, Englehard Model 102 or equivalent (normal crucibles do not work).

Crucible Tongs: Platinum tipped, Englehard model 506.

Blast Burner: 4-cm grid diameter with air and gas inlets, Fisher model 03-910-5 or equivalent.

Ring stand and support.

Plastic stirring rods: 3-mm diameter by 10-cm long, rounded ends.

Hot plate: Teflon coated with 40-cm x 80-cm heating surface, Westbend model 240 or 320 (available at most department stores) or equivalent.

Gas: Liquified propane.

Beakers: Pyrex, 250-ml.

Watch glasses: 80-mm diameter.

Volumetric flasks: 100-ml.

Fumehood: Constructed of #316 stainless steel with wash down capabilities to clean the blower, exhaust ducting and interior working area.

Tissue wipers: 1 ply, 22-cm x 12-cm, Kimwipes #57-210 or equivalent.

1.1.2 Reagents

Nitric acid (16N): Reagent grade.

Hydrofluoric acid (50%): Reagent grade.

Sulfuric acid (36N): Reagent grade.

Potassium fluoride (ANHYDROUS): Reagent grade.

Sodium sulfate (anhydrous): Reagent grade.

Silica gel: Reagent grade.

Tracers:

1.1.3 Methodology

WARNING - Wear face shield, rubber gloves and protective clothing.

(1) Weigh 1.0 g of 100 mesh sample in a 40-ml platinum dish.

(2) Wet sample with 0.5 ml. of 16N HNO_3, and warm gently at 100°C on a hotplate until the chemical reaction and frothing have ceased.

(3) Add 1.0 ml each of tracers and evaporate just to dryness. Do not bake the residue.

(4) Add 2 ml of 50% HF and evaporate just to dryness.

(5) Sprinkle 3 g of anhydrous KF uniformly over the residue and mix with a plastic stirring rod. Remove all particles adherring to the rod with half a piece of tissue wiper, crumple it into a ball and place it in the platinum dish.

(6) Carefully ignite the tissue and heat over a blast burner until KF melts. This step takes approximately four to five minutes. If the melt is turbid or highly colored, add 250 mg of pure silica gel and continue fusion to a clear melt.

(7) With a pair of crucible tongs, grasp the outside walls of the dish, roll the melt around the upper walls. The tips of crucible tongs should NEVER be in contact with the inside walls of the platinum dish.

(8) Resume heating until a clear melt is obtained and continue for two minutes.

(9) Cool to room temperature, add 4.5 ml of 36N H_2SO_4 and warm gently on a hot plate until the KF fusion cake dissolves completely.

(10) Heat over blast burner carefully until abundant amounts of H_2SO_4 fumes are evolved.

(11) Add 2 g of anhydrous Na_2SO_4 and continue heating until a clear pyrosulfate melt is obtained.

(12) Use crucible tongs to grasp the outside walls and roll the melt to the upper walls to dissolve any remaining particles.

(13) Cool to room temperature, flex the walls to break loose the cake and place it in a 250 ml beaker.

(14) Add 35 ml of boiling 5% HCl to the dish and leave it on the hot plate for a few minutes to dissolve any cake remaining in the dish. Roll the solution carefully to reach the upper walls.

(15) Pour the solution into the beaker containing the main portion of the fusion cake and place the beaker on the preheated hot plate.

(16) Hold the dish upside down, rinse the inside walls with 15 ml of boiling 5% HCl, using a disposable pipette, into the beaker

directly. Make sure that hot rinses reach all parts of the inside walls by rotating the dish. Use "rubber fingers" to protect hands. The platinum dish should not be placed in the beaker.

(17) Cover the beaker, boil and swirl to dissolve the cake completely.

(18) Cool to room temperature and make up to 100 ml with deionized water.

(19) Pipette aliquots and proceed to Ra-226, isotopic thorium, Pb-210 and uranium determination.

1.2 HF/HNO_3/$HClO_4$ Digestion-Pyrosulfate Fusion Procedure

1.2.1 Apparatus

Fumehood: For perchloric acid use only, constructed of #316 stainless steel with wash down capabilities to clean the blower, exhaust ducting and interior working area.

Hot plate: Teflon coated with 40-cm x 80-cm heating surface, West end model 240 or 340 (available at most department stores) or equivalent.

Teflon beakers: 100-ml made of virgin teflon TFE.

Teflon watch glasses: 65-mm diameter.

Beakers: Pyrex, 250-ml.

Watch glasses: 80-mm diameter.

Erlenmeyer flasks: Pyrex, 250-ml, wide-mouth.

Volumetric flasks: 100-ml.

Blast burner: 4-cm grid diameter with air and gas inlets, Fisher model 03-910-5 or equivalent.

Flask tongs: Fisher model 10-062 or equivalent.

1.2.2 Reagents

Hydrofluoric acid (50%): Reagent grade.

Nitric acid (16N): Reagent grade.

Perchloric acid (70%): Reagent grade.

Hydrochloric acid (12N): Reagent grade.

Sodium sulfate (anhydrous): Reagent grade.

Potassium sulfate (anhydrous): Reagent grade.

Tracers:

1.2.3 Methodology

(1) Weigh 1.0 g of 100 mesh sample into a 100-ml teflon TFE beaker.

(2) Add 5 ml each of 16N NHO_3 and 50% HF, 2 ml of 70% $HClO_4$, 1.0 ml each of Tracers and cover with a teflon watch glass.

(3) In a perchloric acid fumehood, digest at 100°C on the teflon coated hot plate until sample dissolves.

(4) Remove watch glass and evaporate to perchloric acid fume.

(5) Wash down the walls with 5 ml of 36N H_2SO_4, mix and fume for 10-15 minutes. At this time, the solution no longer wets the sides of the beaker and rolls around the bottom of the beaker like a pool of mercury. The solution can be poured out quantitatively without rinsing.

(6) Roll the solution around to collect isolated droplets and pour into a 250-ml Erlenmeyer flask containing 2 g of anhydrous Na_2SO_4 and 5 g of anhydrous K_2SO_4.

(7) Quickly evaporate over a blast burner to a clear pyrosulfate melt. Cool.

(8) Add 20 ml of boiling 3N HCl, swirl and boil for 5 minutes. Cool, make up to 100 ml with deionized water.

(9) Pipet aliquots and proceed to Ra-226, isotopic thorium, Pb-210 and uranium determination.

1.3 $HF/HNO_3/HClO_4$ Digestion Procedure

1.3.1 Apparatus

See 1.2.1

1.3.2 Reagents

See 1.2.2

1.3.3 Methodology

(1) Follow steps 1 to 4 and 8 of 1.2.3.

(2) Filter the solution through Whatman #1 and save the residue/filter for KF/pyrosulfate fusion.

(3) Pipet aliquots and proceed to Ra-226, thorium isotopes, Pb-210 and uranium determination.

1.4 Sodium Carbonate Fusion Procedure

1.4.1 Apparatus

Muffle Furnace: Variable temperature control.

Platinum crucible: 30-ml capacity.

Hot plate or Steam bath

Beakers: Pyrex, 250-ml.

Watch glasses: 80-mm diameter.

Volumetric flasks: 100-ml.

1.4.2. Reagent

Sodium Carbonate: Reagent grade.

Hydrochloric Acid (12N): Reagent grade.

Tracers:

1.4.3 Methodology

(1) Weigh 1.0 g of 100 mesh sample into platinum crucible.

(2) Add 5 g of sodium carbonate to the sample and mix with stirring rod.

(3) Sprinkle 1 g of sodium carbonate evenly on top of the mixture.

(4) Add 1 ml each of tracers.

(5) Place crucible and content in muffle furnace at room temperature.

(6) Increase muffle furnace temperature to 900°-950°C and fuse for 1 hour.

(7) Remove crucible, cool to room temperature and place on its side in a 250-ml beaker.

(8) Add 60-70 ml deionized water, cover with watch glass and heat gently on a hot plate or steam bath or leave standing at room temperature overnight to disintegrate the contents.

(9) Remove crucible with a pair of tweezers and rinse with deionized water, into the beaker.

(10) Add 10-12 ml of 12N HCl slowly and heat gently until the evolution of carbon dioxide ceases. Cool solution to room temperature.

(11) Filter the solution through Whatman #1, dilute to 100 ml with deionized water. Save the residue/filter for KF/pyrosulfate fusion.

(12) Pipet aliquots and proceed to Ra-226, thorium isotopes, Pb-210 and uranium determination.

2. Determination Of Radioisotopes

All methodologies for the determination of Ra-226, thorium isotopes, Pb-210 and uranium are detailed in the CANMET publication[2] entitled "Analytical Methods Manual-National Uranium Tailings Program".

D. RESULTS AND DISCUSSIONS

All five samples were analysed after dissolution by the four methodologies described in Section B. The results obtained for the five radioisotopes and U are tabulated for sample UTS-1 in Tables 1 to 4, for UTS-3 in Tables 5 to 8, for sample UTS-5 in Tables 9 to 12, for sample AECB 2220 in Tables 13 to 16 and for sample AECB 2218 in Tables 17 to 20. All results are expressed in units of BQ/g (U in µg/g). Table 21 summarizes all the data in terms of averages and standard deviations obtained for 6 determinations. Where additional information is available regarding the composition of the samples, particularily for samples UTS-1, UTS-3 and UTS-5, it is presented. The UTS samples were previously analysed under a comprehensive program administered by Energy, Mines and Resources, CANMET[1]. The "accepted" data presented here are the consensus of that study. For samples AECB 2218 and AECB 2220 there were no "accepted" values available. The uranium contents of these samples, in addition to the UTS samples, were measured by delayed neutron activation analysis. These values were taken as a point of reference for evaluating the sample dissolution procedures.

An examination of the data presented in Table 21 reveals several points:

(1) For the three UTS samples and two AECB samples the dissolution procedure that gives the highest recovery of uranium is the KF/pyrosulfate fusion and the three acid dissolution procedure. The results shown indicate that with this fusion technique, the recovery of uranium ranges between 80% and 120% of the "accepted"

Uranium Recoveries, %

	UTS-1	UTS-3	UTS-5	AECB 2218	AECB 2220
KF/pyro	116	98	92	81	476
Na-Carb	81	66	85	91	143
3 Acid	98	87	78	93	162
Acid/Pyro	67	81	73	65	114

value while with the three acid procedure the recoveries ranged between 78% and 98%. The sodium carbonate fusion and the three acid/pyrosulfate fusion method gave recoveries that were less

TABLE 1: Results of the analysis of UTS-1 after Dissolution by KF/Pyrosulfate Fusion

		Activity, BQ/g				
	U, µg/g	Ra-226	Th-230	Pb-210	Th-232	Th-228
	58	3.44±0.15	2.89±0.16	2.00±0.15	0.21±0.02	0.22±0.02
	68	3.10±0.15	3.22±0.18	2.42±0.16	0.25±0.02	0.24±0.02
	49	3.59±0.14	3.73±0.18	1.78±0.09	0.18±0.02	0.19±0.02
	54	3.70±0.14	3.03±0.16	1.66±0.13	0.35±0.03	0.38±0.04
	57	3.98±0.16	3.34±0.17	2.52±0.17	0.19±0.02	0.25±0.04
	50	3.37±0.15	3.13±0.19	2.76±0.16	0.22±0.02	0.25±0.03
Average	56	3.53	3.22	2.19	0.23	0.26
±1σ	7	0.30	0.29	0.44	0.06	0.06

TABLE 2: Results of Sample UTS-1 Analysis after Sample Dissolution by Sodium Carbonate Fusion

		Activity, BQ/g				
	U, µg/g	Ra-226	Th-230	Pb-210	Th-232	Th-228
	30	3.51±0.03	3.25±0.04	3.46±0.19	0.22±0.03	0.18±0.02
	51	3.55±0.14	3.33±0.16	3.54±0.19	0.26±0.02	0.18±0.02
	35	3.56±0.16	3.36±0.19	2.96±0.18	0.31±0.03	0.18±0.02
	32	3.47±0.18	3.10±0.22	4.82±0.23	0.25±0.04	0.22±0.04
	35	5.45±0.23	3.60±0.19	4.52±0.22	0.28±0.03	0.20±0.03
	49	3.78±0.17	3.74±0.21	3.26±0.19	0.23±0.03	0.18±0.02
Average	39	3.57	3.40	3.76	0.26	0.19
±1σ	9	0.12	0.23	0.73	0.03	0.02

TABLE 3: Results of Sample UTS-1 Analysis after Dissolution by Hydrofluoric, Nitric and Perchloric Acids

		Activity, BQ/g				
	U, µg/g	Ra-226	Th-230	Pb-210	Th-232	Th-228
	48.6	3.71±0.15	3.76±0.19	2.84±0.17	0.21±0.03	0.30±0.04
	40.5	1.33±0.11	7.83±0.59	2.84±0.17	0.31±0.04	0.36±0.04
	47.2	1.41±0.08	4.10±0.20	2.30±0.15	0.21±0.03	0.34±0.04
	54.0	3.32±0.16	3.69±0.21	3.01±0.18	0.28±0.02	0.35±0.04
	47.2	3.22±0.14	4.05±0.21	2.99±0.20	0.26±0.03	0.30±0.04
	45.9	3.42±0.18	3.27±0.21	2.40±0.18	0.06±0.03	0.34±0.03
Average	47.2	2.74	4.45	2.73	0.26	0.33
±1σ	4.4	1.07	1.68	0.30	0.04	0.03

TABLE 4: Results of the Analysis of UTS-1 after Dissolution by Hydrofluoric, Nitric, Perchloric Acids - Pyrosulfate fusion

		Activity, BQ/g				
	U, µg/g	Ra-226	Th-230	Pb-210	Th-232	Th-228
	31	3.02±0.18	2.10±0.02	1.6 ±0.2	0.70±0.08	0.49±0.09
	29	3.15±0.18	2.09±0.02	3.1 ±0.3	0.40±0.04	0.47±0.08
	31	3.55±0.18	2.44±0.02	2.2 ±0.2	0.11±0.02	0.49±0.09
	32	3.5 ±0.2	2.03±0.02	2.8 ±0.3	0.25±0.02	0.36±0.08
	37	3.4 ±0.2	2.79±0.19	2.4 ±0.3	0.30±0.06	0.31±0.06
	32	3.6 ±0.3	2.70±0.20	2.8 ±0.3	0.23±0.06	0.29±0.06
Average	32	3.37	2.4	2.5	0.33	0.40
±1σ	3	0.23	0.3	0.5	0.20	0.09

TABLE 5: Results of the Analysis of UTS-3 after Dissolution by KF/Prysulfate Fusion

		Activity, BQ/g				
	U, µg/g	Ra-226	Th-230	Pb-210	Th-232	Th-228
	486	13.5±0.3	14.9±0.4	11.8±0.4	0.20±0.02	0.12±0.02
	567	13.7±0.3	14.1±0.4	11.4±0.4	0.36±0.04	0.18±0.02
	513	14.3±0.3	15.0±0.5	15.3±0.5	0.25±0.02	0.15±0.02
	594	13.0±0.3	15.7±0.4	10.9±0.4	0.20±0.02	0.17±0.02
	500	13.1±0.3	15.8±0.4	12.0±0.4	0.22±0.02	0.15±0.02
	526	11.8±0.3	14.2±0.2	10.5±0.4	0.20±0.02	0.13±0.03
Average	531	13.23	14.9	12.0	0.24	0.15
±1σ	41	0.84	0.7	1.7	0.06	0.02

TABLE 6: Results of the Analysis of UTS-3 After Dissolution by Sodium Carbonate

		Activity, Bq/g				
	U, µg/g	Ra-226	Th-230	Pb-210	Th-232	Th-228
	392	13.5±0.3	3.9±0.2	12.4±0.4	0.14±0.02	0.07±0.02
	311	14.2±0.4	9.4±0.3	14.4±0.4	0.19±0.02	0.08±0.02
	392	12.0±0.3	9.1±0.2	14.2±0.4	0.13±0.02	0.09±0.02
	324	13.4±0.2	6.3±0.2	18.2±0.5	0.26±0.03	0.06±0.02
	378	13.5±0.3	8.2±0.2	16.8±0.5	0.15±0.02	0.07±0.02
	351	13.0±0.2	8.4±0.2	14.3±0.4	0.11±0.02	0.07±0.02
Average	358	13.3	8.4	15.0	0.16	0.07
±1σ	35	0.7	1.1	2.1	0.05	0.01

TABLE 7: Results of the Analysis of UTS-3 After Dissolution by Hydrofluoric, Nitric and Perchloric Acids

		Activity, BQ/g				
	U, µg/g	Ra-226	Th-230	Pb-210	Th-232	Th-228
	486	11.0±0.2	14.6±0.3	10.1±0.3	0.41±0.05	0.25±0.03
	499	12.5±0.3	14.4±0.5	10.3±0.4	0.20±0.02	0.22±0.02
	432	13.0±0.3	16.4±0.8	9.1±0.3	0.26±0.03	0.24±0.03
	446	12.1±0.3	15.3±0.7	11.3±0.4	0.30±0.03	0.25±0.03
	527	12.8±0.3	15.4±0.4	11.0±0.4	0.28±0.03	0.30±0.03
	418	13.0±0.4	16.5±0.7	9.3±0.3	0.20±0.03	0.25±0.03
Average	468	12.4	15.4	10.2	0.27	0.25
±1σ	42	0.8	0.9	0.9	0.07	0.03

TABLE 8: Results of the Analysis of UTS-3 after Dissolution by Hydrofluoric, Nitric, Perchloric Acids - Pyrosulfate fusion.

		Activity, BQ/g				
	U, µg/g	Ra-226	Th-230	Pb-210	Th-232	Th-228
	382	14.9±0.6	9.1 ±0.4	10.0±0.6	0.16±0.04	0.05±0.02
	330	11.4±0.5	8.01±0.02	9.2±0.6	0.07±0.04	0.04±0.02
	480	13.2±0.6	7.6 ±0.4	12.0±0.7	0.16±0.06	0.04±0.02
	458	13.5±0.6	7.8 ±0.4	11.8±0.7	0.37±0.08	0.04±0.02
	458	13.3±0.5	7.8 ±0.3	11.1±0.7	0.42±0.07	0.07±0.02
	518	13.3±0.6	7.4 ±0.4	12.1±0.7	0.42±0.10	0.09±0.02
Average	438	13.3	8.0	11.0	0.27	0.06
±1σ	69	1.1	0.6	1.2	0.15	0.02

TABLE 9: Results of the Analysis of UTS-5 After Dissolution by KF/Pyrosulfate Fusion

		Activity, BQ/g				
	U, µg/g	Ra-226	Th-230	Pb-210	Th-232	Th-228
	1,175	14.9±0.3	13.4±0.3	13.4±0.4	0.9±0.2	1.0±0.2
	1,188	13.7±0.3	14.1±0.4	12.8±0.4	0.9±0.2	0.9±0.2
	1,242	13.6±0.3	14.0±0.4	11.8±0.4	0.9±0.2	1.1±0.2
	1,134	15.0±0.3	14.3±0.4	12.5±0.4	1.0±0.2	1.1±0.2
	1,202	15.0±0.3	11.4±0.3	11.0±0.4	1.0±0.2	0.8±0.2
	1,175	14.1±0.4	11.9±0.4	9.5±0.3	1.0±0.1	0.9±0.2
Average	1,186	14.4	13.2	4.8	0.95	1.0
±1σ	36	0.7	1.2	1.4	0.05	0.1

TABLE 10: Results of the Analysis of UTS-5 After Dissolution by Sodium Carbonate Fusion

		Activity, BQ/g				
	U, µg/g	Ra-226	Th-230	Pb-210	Th-232	Th-228
	1012	14.4±0.3	14.5±0.5	14.4±0.6	0.85±0.15	0.94±0.12
	1121	13.4±0.3	10.4±0.5	12.9±0.6	0.73±0.17	0.80±0.18
	-	13.6±0.3	7.7±0.4	-	-	-
	999	15.1±0.3	15.5±0.6	14.6±0.6	0.83±0.10	1.2 ±0.15
	1094	13.7±0.3	16.5±0.7	14.1±0.6	0.72±0.15	1.2 ±0.18
	1242	-	-	16.4±0.7	0.35±0.14	1.9 ±0.15
Average	1094	14.0	12.9	14.5	0.75	1.2
±1σ	98	0.7	3.7	1.3	0.22	0.4

TABLE 11: Results of the Analysis of UTS-5 after Dissolution by Hydrofluoric, Nitric and Perchloric Acids

		Activity, BQ/g				
U, µg/g		Ra-226	Th-230	Pb-210	Th-232	Th-228
	932	15.4±0.4	10.9±0.4	9.0 ±0.3	2.0±0.2	1.0±0.1
	1080	16.6±0.4	13.0±0.5	9.6 ±0.3	2.4±0.3	1.5±0.2
	986	14.2±0.3	14.7±0.4	12.8±0.4	1.5±0.2	1.2±0.2
	972	14.5±0.4	17.1±0.6	13.3±0.4	1.5±0.2	0.8±0.2
	1080	13.7±0.3	11.6±0.4	12.4±0.4	2.0±0.2	1.5±0.2
	1026	10.2±0.3	11.1±0.4	14.8±0.3	1.7±0.2	1.8±0.2
Average	1013	14.1	13.1	12.0	1.8	1.3
±1σ	60	2.2	2.4	2.2	0.4	0.4

TABLE 12: Results of the Analysis of UTS-5 after Dissolution by Hydrofluoric, Nitric, Perchloric Acids - Pyrosulfate Fusion

		Activity, BQ/g				
	U, µg/g	Ra-226	Th-230	Pb-210	Th-232	Th-228
	975	16.6±0.6	9.2±0.3	12.6±0.7	0.62±0.08	1.06±0.10
	1012	17.0±0.7	8.6±0.4	15.0±0.8	0.84±0.11	1.05±0.10
	802	18.0±0.7	9.1±0.4	11.0±0.7	0.96±0.12	1.39±0.14
	788	15.1±0.6	8.2±0.3	13.3±0.8	1.08±0.12	1.24±0.13
	1012	14.4±0.6	9.0±0.4	12.2±0.7	1.09±0.14	0.42±0.16
	975	15.2±0.6	9.5±0.4	11.3±0.7	1.22±0.14	1.05±0.2
Average	937	16.1	8.9	12.6	0.97	1.2
±1σ	92	1.4	0.5	1.5	0.21	0.2

TABLE 13: Results of the Analysis of AECB 2220 after Dissolution by KF/Pyrosulfate Fusion

		Activity, BQ/g				
	U, µg/g	Ra-226	Th-230	Pb-210	Th-232	Th-228
	8.8	0.160±0.006	0.305±0.009	≤0.3	0.015±0.002	0.014±0.002
	3.9	0.212±0.008	0.265±0.007	≤0.3	0.010±0.002	0.017±0.002
	16.9	0.715±0.013	0.258±0.015	≤0.3	0.010±0.002	0.012±0.003
	10.9	0.182±0.007	0.273±0.008	≤0.4	0.011±0.002	0.033±0.003
	12.2	0.171±0.007	0.264±0.007	≤0.3	0.014±0.002	0.018±0.002
	4.1	0.187±0.006	0.261±0.007	≤0.3	0.016±0.002	0.026±0.002
Average	9.5	0.181	0.271	≤0.3	0.013	0.020
±1σ	5.0	0.018	0.017	-	0.003	0.008

TABLE 14: Results of the Analysis of AECB 2220 after Dissolution by Sodium Carbonate Fusion

		Activity, BQ/g				
	U, µg/g	Ra-226	Th-230	Pb-210	Th-232	Th-228
	3.9	0.244±0.006	0.300±0.007	0.72±0.07	0.014±0.002	0.013±0.002
	4.4	0.246±0.006	0.294±0.006	0.95±0.09	0.014±0.001	0.017±0.002
	5.0	0.232±0.006	0.285±0.007	0.10±0.10	0.019±0.002	0.017±0.002
	1.1	0.190±0.006	0.283±0.007	1.21±0.10	0.029±0.002	0.010±0.002
	1.0	0.169±0.006	0.245±0.007	1.41±0.11	0.035±0.003	0.007±0.003
	1.3	0.261±0.007	0.219±0.008	1.38±0.11	0.021±0.002	0.070±0.002
Average	2.8	0.22	0.283	1.1	0.022	0.014
±1σ	1.8	0.04	0.019	0.3	0.008	0.005

TABLE 15: Results of the Analysis of AECB 2220 after Dissolution by Hydrofluoric, Nitric and Perchloric Acids

		Activity, BQ/g				
	U, µg/g	Ra-226	Th-230	Pb-210	Th-232	Th-228
	6.9	0.198±0.009	0.379±0.012	≤0.3	0.018±0.003	0.011±0.002
	4.1	0.63 ±0.05	0.378±0.012	≤0.3	0.023±0.003	0.013±0.003
	2.6	0.74 ±0.05	0.324±0.011	≤0.3	0.048±0.004	0.016±0.003
	2.0	1.14 ±0.07	0.323±0.011	≤0.3	0.031±0.004	0.016±0.003
	2.4	0.121±0.018	0.278±0.016	≤0.3	0.031±0.006	0.031±0.003
	2.1	0.105±0.010	≤0.005	≤0.3	0.023±0.006	0.041±0.003
Average	3.4	0.50	0.34	≤0.3	0.029	0.021
±1σ	1.9	0.41	0.04	≤0.3	0.011	0.012

TABLE 16: Results of the Analysis of AECB 2220 after Dissolution by Hydrofluoric, Nitric, Perchloric Acids-Pyrosulfate Fusion

		Activity, BQ/g				
	U, µg/g	Ra-226	Th-230	Pb-210	Th-232	Th-228
	3.3	0.09 ±0.02	0.26±0.04	1.26±0.17	0.027±0.009	≤0.005
	1.4	0.12 ±0.03	0.28±0.06	1.04±0.14	0.012±0.005	≤0.005
	2.8	0.07 ±0.02	0.13±0.04	1.40±0.18	0.024±0.012	≤0.005
	2.1	0.14 ±0.03	0.20±0.04	1.26±0.17	0.026±0.009	≤0.005
	2.2	0.08 ±0.02	0.28±0.02	0.77±0.11	0.009±0.005	≤0.005
	2.1	0.12 ±0.04	0.23±0.02	1.04±0.14	0.013±0.002	≤0.005
Average	2.4	0.10	0.23	1.1	0.018	≤0.005
±1σ	0.8	0.03	0.06	0.2	0.008	0.005

TABLE 17: Results of the Analysis of AECB 2218 after Dissolution by KF/Pyrosulfate Fusion

		Activity, BQ/g				
	U, µg/g	Ra-226	Th-230	Pb-210	Th-232	Th-228
	9.45	0.79±0.05	1.90±0.07	2.72±0.15	0.068±0.014	0.022±0.008
	5.94	0.81±0.05	1.44±0.05	2.47±0.15	0.060±0.010	0.015±0.006
	4.79	0.80±0.04	1.85±0.06	1.55±0.13	0.064±0.010	0.022±0.006
	3.04	0.71±0.03	1.89±0.05	0.33±0.03	0.040±0.007	0.034±0.007
	4.32	0.76±0.03	1.94±0.06	1.95±0.13	0.054±0.010	0.020±0.006
	5.47	0.79±0.03	1.86±0.05	3.22±0.18	0.035±0.006	0.032±0.006
Average	5.5	0.78	1.81	2.0	0.054	0.024
±1σ	2.2	0.04	0.19	1.0	0.013	0.007

TABLE 18: Results of the Analysis of AECB 2218 after Dissolution by Sodium Carbonate Fusion

		Activity, BQ/g				
	U, µg/g	Ra-226	Th-230	Pb-210	Th-232	Th-228
	5.7	0.91±0.03	1.86±0.05	1.22±0.10	0.130±0.010	0.125±0.012
	6.1	0.85±0.04	2.07±0.08	0.93±0.09	0.058±0.013	0.080±0.015
	6.8	0.92±0.02	2.04±0.04	0.94±0.09	0.107±0.009	0.043±0.006
	5.9	0.84±0.03	2.07±0.05	0.82±0.08	0.152±0.015	0.141±0.014
	14.9	0.88±0.04	2.01±0.06	1.02±0.09	0.157±0.016	0.189±0.017
	6.3	0.85±0.02	1.94±0.05	0.73±0.08	0.079±0.009	0.177±0.017
Average	6.2	0.88	2.00	0.94	0.11	0.13
±1σ	0.4	0.03	0.08	0.17	0.04	0.06

TABLE 19: Results of the Analysis of AECB 2218 after Dissolution by Hydrofluoric, Nitric and Perchloric Acids

		Activity, BQ/g				
	U, µg/g	Ra-226	Th-230	Pb-210	Th-232	Th-228
	3.62	0.84±0.04	2.48±0.17	0.89±0.07	0.06±0.02	0.10±0.02
	11.1	0.81±0.04	2.09±0.13	≤0.3	0.13±0.02	0.04±0.02
	9.0	0.89±0.04	2.08±0.11	≤0.3	0.13±0.02	0.04±0.02
	4.0	0.71±0.03	2.50±0.15	≤0.3	0.08±0.02	0.06±0.02
	4.0	0.85±0.04	1.95±0.08	≤0.3	0.07±0.02	0.03±0.01
	6.1	0.41±0.03	2.04±0.07	-	0.10±0.03	0.02±0.01
Average	6.3	0.75	2.19	≤0.3	0.10	0.05
±1σ	3.1	0.18	0.24	-	0.03	0.03

TABLE 20: Results of the Analysis of AECB 2218 after Dissolution by Hydrofluoric, Nitric, Perchloric Acids-Pyrosulfate Fusion

		Activity, BQ/g				
	U, µg/g	Ra-226	Th-230	Pb-210	Th-232	Th-228
	4.2	0.81±0.08	1.54±0.10	1.56±0.19	0.09±0.02	0.08±0.02
	4.9	0.78±0.10	1.81±0.14	1.57±0.19	0.11±0.02	0.10±0.02
	1.4	0.83±0.10	1.63±0.11	1.8 ±0.2	0.10±0.02	0.10±0.02
	7.4	0.95±0.10	1.74±0.12	0.80±0.12	0.14±0.02	0.15±0.02
	5.1	0.81±0.05	1.48±0.07	1.12±0.15	0.14±0.02	0.12±0.02
	3.5	0.79±0.08	1.49±0.16	0.94±0.13	0.12±0.03	0.12±0.03
Average	4.4	0.83	1.62	1.3	0.12	0.11
1	2.0	0.06	0.13	0.4	0.02	0.02

TABLE 21: Results of the Determination of the Radionuclides Content of Solids Using Four Methods of Sample Dissolution.

	U, µg/g	Ra-226	Th-230	Pb-210	Th-232	Th-228
		BQ/g				
UTS-1						
KF/Pyro	56± 7	3.5 ± 0.3	3.2 ± 0.3	2.2± 0.4	0.23 ±0.06	0.26 ±0.06
Na-Carb.	39± 9	3.57± 0.12	3.4 ± 0.2	3.8± 0.7	0.26 ±0.03	0.19 ±0.02
3 Acid	47± 4	2.7 ± 1.1	4.4 ± 1.7	2.7± 0.3	0.26 ±0.04	0.33 ±0.03
Acid/Pyro	32± 3	3.4 ± 0.2	2.4 ± 0.3	2.5± 0.5	0.33 ±0.20	0.40 ±0.09
Accepted	48*	3.5 - 3.8	3.0 - 4.2	3.2 - 3.6	0.6 - 0.8	0.6 - 0.8
		(3.67±0.15)	(3.4 ± 0.2)	(3.4± 0.2)	(0.68 ±0.10)	(0.68 ±0.12)
UTS-3						
KF/Pyro	531±41	13.2 ± 0.8	14.9 ± 0.7	12.0± 1.7	0.24 ±0.06	0.15 ±0.02
Na-Carb.	358±35	13.3 ± 0.7	8.4 ± 1.1	15.0± 2.1	0.16 ±0.05	0.07 ±0.01
3 Acid	468±42	12.4 ± 0.8	15.4 ± 0.9	10.2± 0.9	0.27 ±0.07	0.25 ±0.03
Acid/Pyro	438±69	13.3 ± 0.7	8.0 ± 0.6	11.0± 1.2	0.27 ±0.15	0.06 ±0.02
Accepted	540*	12.7 - 13.9	10.5 - 12.1	11.7-15.5	N.A.	N.A.
		(13.2 ± 0.8)	(11.3 ± 0.8)	(12.6± 0.9)	(0.16 ±0.04)	(N.A.)
UTS-5						
KF/Pyro	1186±36	14.4 ± 0.7	13.2 ± 1.2	11.8± 1.4	0.95 ±0.05	1.0 ±0.1
Na-Carb.	1094±98	14.0 ± 0.7	12.9 ± 3.7	14.5± 1.3	0.75 ±0.22	1.2 ±0.4
3 Acid	1013±60	14.1 ± 2.2	13. ± 2.	12. ± 2.	1.8 ±0.4	1.3 ±0.4
Acid/Pyro	937±92	16.1 ± 1.4	8.9 ± 0.5	12.6± 1.5	0.97 ±0.4	1.2 ±0.4
Accepted	1290±26*	14.5 - 20.0	13.0 - 18.2	11.4-17.7	1.7 ±2.4	1.7 ±2.5
		(16.5 ± 0.6)	(14.5 ± 0.6)	(14.0± 0.6)	(N.A.)	(N.A.)
AECB 2218						
KF/Pyro	5.5±2.2	0.78± 0.04	1.81± 0.19	2.0 ±1.0	0.054±0.013	0.024±0.007
Na-Carb.	6.2±0.4	0.88± 0.03	2.00± 0.08	0.94±0.17	0.11 ±0.04	0.13 ±0.06
3 Acid	6.3±3.1	0.75± 0.18	2.19± 0.24	≤0.3	0.10 ±0.03	0.05 ±0.03
Acid/Pyro	4.4±2.0	0.83± 0.06	1.62± 0.13	1.3 ±0.4	0.12 ±0.02	0.11 ±0.03
Accepted	6.8*					
AECB 2220						
KF/Pyro	10 ±5	0.181±0.018	0.271±0.017	≤0.3	0.013±0.003	0.020±0.008
Na-Carb.	3 ±2	0.22 ±0.04	0.288±0.019	1.1 ±0.3	0.022±0.008	0.014±0.005
3 Acid	3.4±1.9	0.5 ±0.4	0.34 ±0.04	≤0.3	0.029±0.011	0.021±0.012
Acid/Pyro	2.4±0.8	0.10 ±0.03	0.23 ±0.06	1.1 ±0.2	0.018±0.008	≤0.005
Accepted	2.1*					

*by Delayed Neutron Activation Analysis, AECL, Ottawa.

consistent and about 10% lower. Results for uranium obtained with sample AECB 2220 varied considerably and were attributed to possible sample inhomogeneity.

(2) For Radium-226, calculations of the recoveries based on the "accepted" values of the UTS samples show that all methods of

Radium-226 Recoveries

	UTS 1	UTS 3	UTS 5
KF/Pyro	95%	99%	87%
NA Carb.	97%	100%	87%
3 Acid	74%	93%	85%
Acid/pyro	93%	100%	111%

sample dissolution except the three acid dissolution method gave greater than 85% recovery for all samples. The latter method was relatively poor for UTS-1 giving only 74% recovery of the Ra-226 present.

Comments regarding the best methods of dissolution for radium 226 in samples AECB 2218 and 2220 are difficult because of the lack of a comparison. However, for sample AECB 2218 all four methods gave comparable results. With sample 2220 the radium-226 results varied widely depending on the dissolution method used. This behaviour is not unlike the observations made concerning the uranium data in (1) above.

(3) For thorium, in particular Th-230, the KF/pyrosulfate and sodium carbonate fusion methods gave results that were, for the most part, close to 100% recovery.

Thorium-230 Recoveries

	UTS 1	UTS 3	UTS 5
KF/Pyro	94%	132%	91%
Na Carb.	100%	74%	90%
3 Acid	129%	136%	90%
Acid/pyro			

The three acid dissolution procedure by itself gave results that tended to be high while the 3 acid/pyrosulfate combination gave results that tended to be lower than expected.

The levels of Th-230 in sample AECB 2218 and 2220 were all found to be in agreement regardless of the manner in which the sample was dissolved.

(4) For Lead-210 the four methods gave results that varied by a large amount. The most consistent recoveries appeared to be

Lead-210 Recovery

	UTS 1	UTS 3	UTS 5
KF/pyro	65%	95%	84%
Na Carb	112%	119%	82%
3 Acid	79%	81%	79%
Acid/pyro	74%	87%	90%

obtained with the three acid dissolution procedure combined with the pyrosulfate fusion.

The most interesting observation for the Pb-210 determination was that the recoveries obtained, after KF/pyrosulfate and sodium carbonate fusions in platinum dishes, were not as low as might be expected if the lead electroplated onto the platinium. This phenomenon is quoted frequently in the literature.

The Pb-210 results obtained for samples AECB 2218 and 2220 varied widely. In view of the relatively consistent behaviour of U, Ra-226 and Th-230 in those samples an explanation is not obvious.

Attempts were made to relate the fraction of sample that dissolved during each dissolution procedure to the recovery of each individual isotope of interest. This proved to be difficult for a number of reasons.

(1) The KF/pyrosulfate fusion and the three acid/pyrosulfate fusion gave imperceivable amounts of residues. The third method, sodium carbonate gave a residue that was deduced to be hydrolysed silica. Because of its nature and mass expansion, quantification of the amount of residue that remained was considered to be meaningless. In all instances more residue weight was found than sample weight fused. The fourth method of sample dissolution was the three acid dissolution procedure. The relative amounts of residue obtained are reported in Table 22 for the five samples examined. It shows that the

TABLE 22 - Fraction of Sample Not Soluble In Hydrofluoric, Nitric, Perchloric Acid. - average of 6 measurements.

Identification	Sample Undissolved, %
UTS 1	21±11
UTS 3	26±12
UTS 5	17± 5
AECB 2218	26±11
AECB 2220	20±20

amounts observed were generally not consistent within each sample and wide sample variations were observed. However, these variations did not appear to be similarily reflected in the radioisotopes analysis data. That is, much better precision for Ra-226 and U measurements were obtained than might be expected, based on the wide variation in residue. Also, the recoveries of each radioisotope could not be correlated with the insoluble portions.

This study was able to show that the KF/pyrosulfate fusion dissolution procedure is the fastest method to be applied to the analysis of 10-15 samples or less. Using this procedure, that number of samples can be dissolved and made ready for radiochemical analysis within 6 to 8 hours. Using the other three dissolution methodologies requires between 2 and 2.5 days to arrive at the same situation. When 20-30 samples or more require analysis then the speed advantage is lost. In that case, the KF/pyrosulfate or the three acid dissolution method followed by pyrosulfate fusion are the recommended procedures because the analytical data obtained have been generally shown by this study, to be the most accurate and precise.

E. REFERENCES

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